

Phthalates in the Charles and the Merrimack Rivers

by Ronald A. Hites*

The identification and quantification of individual organic compounds in polluted water has been recognized as a prerequisite to rational pollution abatement planning (1). In the past, this information has been difficult to obtain primarily due to the lack of suitable analytical methods. The last several years, however, have seen the development of powerful organic analytical techniques which are suitable for the complex mixtures that are to be expected from polluted water. Premier among these methods is computerized combined gas chromatography-mass spectrometry (GC/MS). We have applied this technique, as well as high-pressure liquid chromatography (LC), to a study of the lipophilic organic compounds present in the Charles and Merrimack rivers.

The lipophilic organic compounds were extracted from river water with methylene chloride. The solvent layer was separated and evaporated under reduced pressure. This extract was then analyzed by GC/MS. Details of the sampling and extraction procedure can be found elsewhere (2). A procedural blank showed only very small amounts of material and was judged acceptable. The mass spectral data were interpreted with various computer-assisted techniques (3-5). Mass chromatograms (plots of the

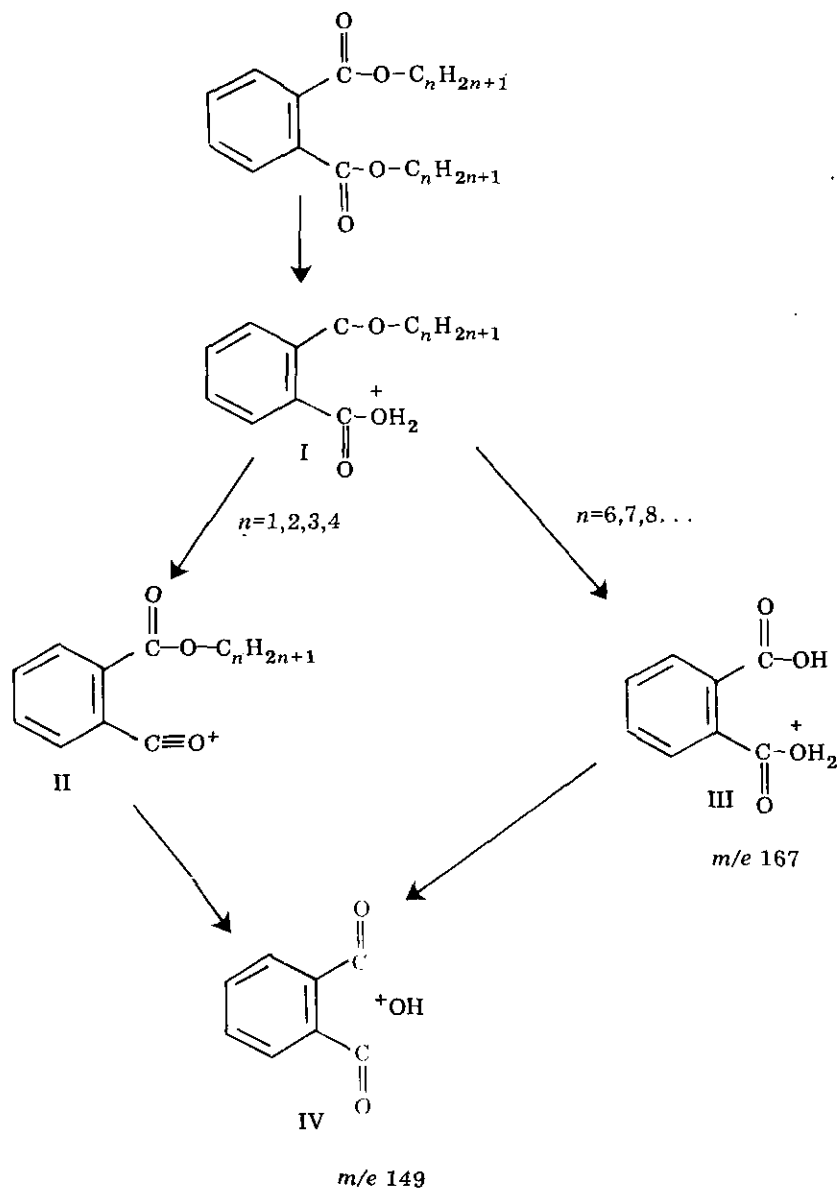
absolute intensity of one mass versus time) were particularly useful for detecting specific compounds or groups of compounds (4).

As a result of these techniques, in addition to various aliphatic and aromatic hydrocarbons (2), several phthalate esters were detected. This report will detail the GC/MS identification and the LC quantification of these compounds.

Because of the importance of the mass spectral evidence in this study, the nature of the mass spectra of phthalate esters (6, 7) will be briefly reviewed (Scheme 1). Upon electron impact all phthalate esters (except dimethyl phthalate) produce a very abundant fragment ion at m/e 149 due to the protonated phthalic anhydride moiety (ion IV in Scheme 1). If the alkyl chain has six carbons or more, an ion of m/e 167 (ion III) is also produced. For small alkyl chains (4 carbon atoms or less) ions at m/e 163, 177, 191, or 205 (for $n = 1, 2, 3$, or 4, respectively) (ions II) predominate instead of m/e 167. Another important fragment ion is thought to have structure I, which gives ions at m/e 223 for $n = 4$ and at 279 for $n = 8$. Molecular ions are usually of such low abundance that they are not observed.

Since the above ions are characteristic of phthalate esters, their mass chromatograms will show peaks which indicate the presence of these esters; i.e., the mass spectrometer will act as a specific detector for these compounds. As an example, the bottom trace of Figure 1 shows the reconstructed gas chromatogram resulting from an extract

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SCHEME 1. Partial fragmentation pathways for phthalate esters

of water from the Merrimack River. Although this chromatogram is extremely complex, the presence of phthalate esters can be deduced by an examination of the mass chromatograms shown in the top two traces of Figure 1. The trace resulting from m/e 163 (top) suggests the presence of dimethyl phthalate, and that of m/e 149 (middle)

suggests other phthalate esters. An examination of the mass chromatograms of other masses characteristic of phthalates (e.g., m/e 167, 205, 223, or 279) confirms that phthalates are present at spectrum index numbers 110, 133, 195, and 278. Comparison of these mass spectra (Figs. 2 and 3) and gas chromatographic retention times

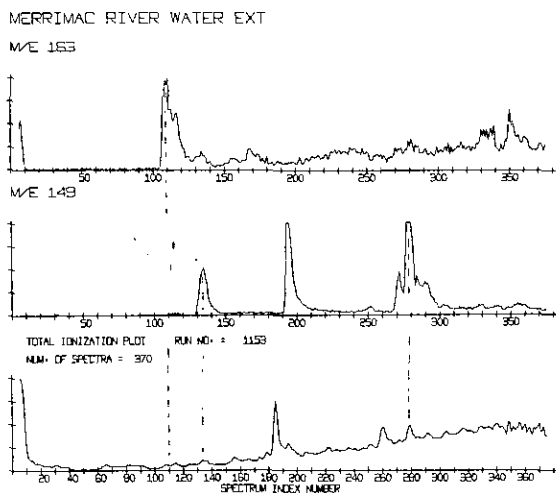


FIGURE 1. Reconstructed gas chromatogram of an extract of water from the Merrimack River (bottom); corresponding mass chromatograms (4) for m/e 149 (middle) and m/e 163 (top). GC conditions: column, 150 x 0.32 cm, 0.1% OV-1 on glass beads; temperature, 70 to 260°C at 8°C/min.

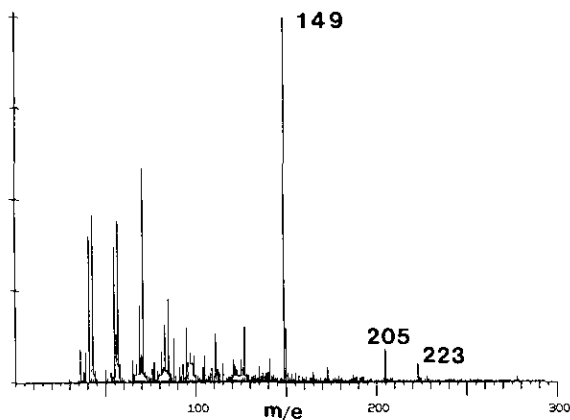


FIGURE 2. Mass spectrum (spectrum index number 195, Fig. 1) of a component from Merrimack River water extract. This spectrum agrees with that of dibutyl phthalate.

with those of authentic material yields the following identifications: dimethyl phthalate (spectrum index 110), diethyl phthalate (spectrum index 133), dibutyl phthalate (spectrum index 195, Fig. 2), and di-2-ethylhexyl phthalate (spectrum index 278, Figure 3). Similar data for extracts of water from the Charles River (Boston) (Figs. 4 and 5) enable one to identify dibutyl phthalate

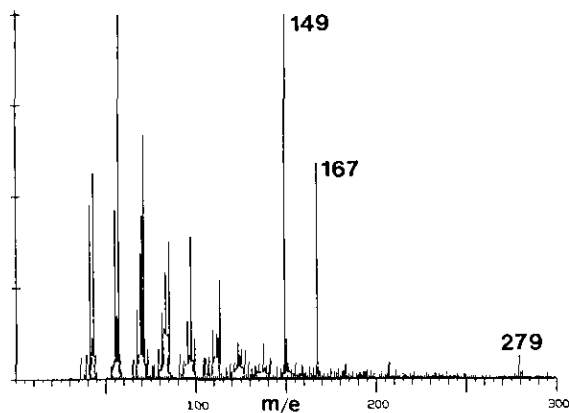


FIGURE 3. Mass spectrum (spectrum index number 278, Fig. 1) of a component from Merrimack River water extract. This spectrum agrees with that of di-2-ethylhexyl phthalate.

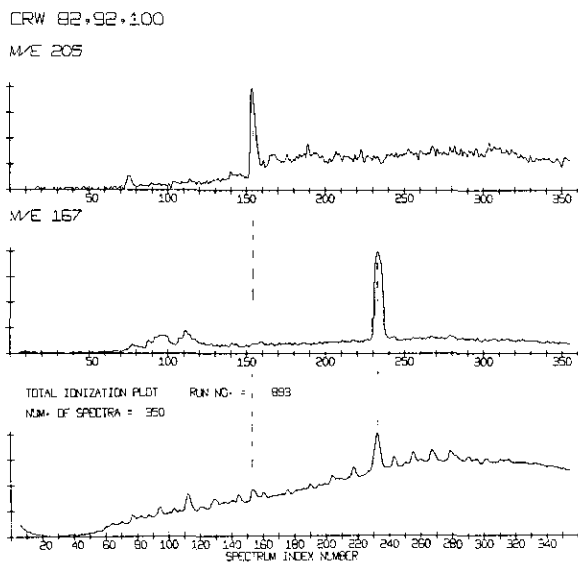


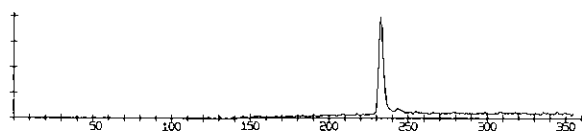
FIGURE 4. Reconstructed gas chromatogram of an extract of water from the Charles River (bottom); corresponding mass chromatograms (4) for m/e 167 (middle) and m/e 205 (top). GC conditions: see Fig. 1.

and di-2-ethylhexyl phthalate at spectrum index numbers 153 and 233, respectively.

Once the presence of phthalate esters was known it was of interest to establish their concentration and distribution in the Charles River. We chose to make this determination by high-pressure, high-speed liquid chromatography operating in the affinity mode, i.e., liquid-solid chromatography. This mode en-

CRW 82,92,100

M/E 279



M/E 223

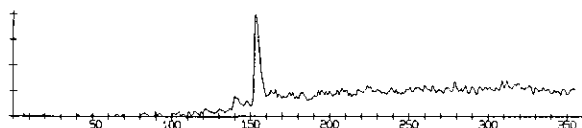


FIGURE 5. Mass chromatograms (4) for m/e 223 (bottom) and m/e 279 (top) from an extract of Charles River water (Fig. 4).

sures that all phthalates are eluted together in one peak regardless of the carbon number of the alkyl groups. An ultraviolet absorption detector at 254 nm served as a sensitive and specific detector for these compounds. A Waters ALC 202 instrument was used. The column, a 120 x 0.32 cm tube packed with Porasil T, was operated at 400 psi and at 23°C with methylene chloride as the liquid phase. For quantification, 0.5 $\mu\text{g/l}$. of acetophenone was added to the river water before extraction. Acetophenone was selected as the internal standard because its retention time was only slightly greater than that of phthalate esters and it elutes in a section of the chromatogram with few interfering peaks (Fig. 6).

The relative concentration of phthalate to acetophenone can be determined from the ratio of their peak areas corrected by the ratio of their absorptivities at 254 nm (2.70 for di-2-ethylhexyl phthalate and 37.6 for acetophenone). Since the extraction efficiencies of acetophenone and phthalate esters are about equal, the relative phthalate concentration can be converted to absolute concentration. Table 1 shows the phthalate concentrations (in duplicate) for several samples taken from the Charles River on May 17, 1972. ("River mile" is the distance of the sampling location from the mouth of the river which is taken to be the Charles River Dam.)

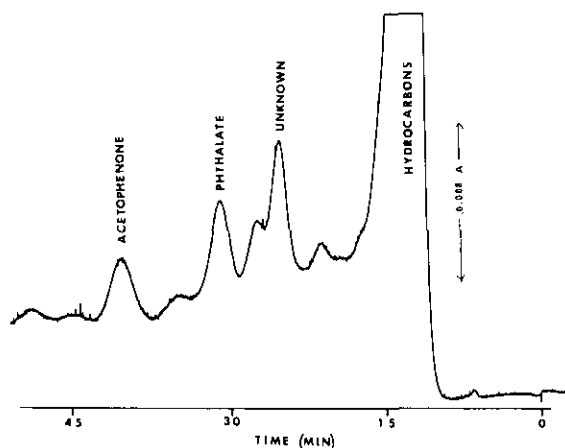


FIGURE 6. Liquid chromatogram of an extract of Charles River water. The acetophenone has been added as an internal standard. See text for LC conditions.

Table 1. Phthalate concentration in the Charles River.

River mile	Depth, ft	Phthalate concn, ppb
7	4	1.9, 1.8
3	4	1.1, 1.1
1	4	0.88, 0.89
1	11	0.97, 0.98

These data show that the phthalate concentration increases as one moves upstream and are in agreement with the following model. Phthalates are added to the river from one or more sources which are located above river mile 7. As this contaminated water flows downstream, more water is added from runoff and other sources, thus diluting the phthalates. In addition, biological activity in this slowly flowing river also tends to reduce the phthalate concentration as the water moves downstream. The two samples taken at river mile 1 but at two different depths differ significantly. This is certainly due to the severe vertical stratification exhibited by the river at this location.

We hope that this work has demonstrated the power of modern analytical methods for the identification and determination of

organic pollutants at the fractional parts per billion level in water. In addition, this study is still another confirmation of the ubiquity of phthalate esters.

Acknowledgement

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